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Risk Mitigation Methods on the Removal of Pesticide Residues in Grapes Fruits for Food Safety.

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ABSTRACT

The study has been designed to determine the extent of pesticide residues removal from Grapes through household processing. For this, Grapes fruits were grown on grape garden and application of pesticidesdimethoate, profenophos, chlorpyrifos, Malathion, phosalone, quinalphos, triazophos, and lambda cyhalothrin were carried out at recommended dosage. After 2 hours, the grapes were collected and labeled and brought to the laboratory of pesticide residues, Professor JayasankarTelangana state Agricultural University, Hyderabad for their analyses and further processing such as washing with tap water, 2% salt solution, 2% tamarind solution, Lemon water, baking soda, vinegar, Bio wash (available in market) and cooking, etc. being practiced at various households processed methods. Pesticide residues were extracted from Grapes solvent partitioning and cleaned by C18 cartridges/activated charcoal by using acetonitrile for elution and then cleaned up residues were analyzed through GC ECD.The analysis of data revealed that Organo phosphate pesticides are highly effective against pests at low dosages. Grapes samples washing with tap water reduced the residues in the range of 37.0-73.2%, Lemon water reduced by residues in the range of 42.5-72.3%, 2% Tamarind solution reduced by residues in the range of 26.1-69.1%, 2% salt solution reduced by residues in the range of 44.3-78.7%, Baking soda reduced by residues in the range of24.0-65.1%, Vinegar reduced by residues in the range of17.1-58.5%.Bio-wash removed by residues in the range of 44.5-75.2%, reduced by residues in the range of 42.9-83.2%. Bio wash of grapes found more effective Followed by 2% salt solution in dislodging the residues.

Keywords: Grapes, Fruits pesticide, processing, residues, washing,

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INTRODUCTION

Grapes is an important commercial horticulture crop Major grape-growing states are Andhra Pradesh , Maharashtra, Karnataka, , Tamil Nadu, and the north-western Region covering Punjab, Haryana, western Uttar Pradesh, Rajasthan and Madhya Pradesh. In Andhra Pradesh Mainly growing in Hyderabad, Ranga Reddy, Mahbubnagar, Anantapur and Medak districts. In Maharashta ranks first in terms of production accounting for more than 82.56% of total production and highest productivity in the country. A wide range of pesticides are used for the better yield of grape due to pest infestation throughout the season of the crop. Pesticides have potential adverse effects on vegetables, fruits, animal resources and human health (Perez Bendito D etal). Because of their widespread use, their toxic residue have been reported in various environmental matrices (Kumari B (1996,2002,2003) etal, Frank R.etal). Thus the determination of pesticide residue in foods and other environmental components/ commodities like water, soil, fruits vegetables and total diet has become an essential requirement for the consumers, producers and authorities for food quality control. Various studies have been done towards the beneficial properties of fruit juice because they have several components such as phenols, vitamins and flavonoids with antioxidant effect. However, fruit juice can also contain residue of pesticide used as standard pest control method in crops. Many of the pesticidesare degraded through oxidative mechanism and their persistence in juice can be enhanced by antioxidants (Pico Y.etal). However, injudicious and indiscriminate use of these highly persistent and toxic chemicals in horticulture caused serious contamination in fruits like grape. The farmers, authorities and exporters are taking care to maintain pesticide residue in the grape belowminimum residue limit (MRL) put by the receiving country by following the precised techniques, proper time period and applying optimum quantity of degradable pesticide etc. during the production of export quality grapes. But most of the farmers, who are interested to sell the grapes in domestic market, bother only about yield of the fruit and economy of the farming and apply the pesticide injudiciously without bothering about MRL. Indiscriminate use of pesticidesparticularly in fruiting stage and non-adoption of safe waiting period leads to accumulation of pesticide residue in consumable fruits and vegetables. Contamination of pesticide residue in vegetables has been reported by several researchers (Kumari B etal,Madan V.K etal). There is no intensive monitoring body to control the pesticide residue limit in the grape of every farm in India. Aim of the study was to evaluate the residue of different chemical group of pesticide: Organochlorines (OC) Synthetic Pyrethriods (SP), Organo-Phosphorous (OP) and Carbamate in grape of the Bijapur district. It ishoped that data will produce awareness among the grape farmers and consumers and establish a base line in determining changes in the residue level of different pesticides in different fruits in future.

The aim of this study was to evaluate the pesticide residues of four different chemical groups i.e., Organophosphorus (OP) in Grapes to assess the effect on residues of some household processes like washing with Tap water, 2% salt solution, 2% tamarind solution, lemon water, Baking soda, Vinegar, Bio wash(available in market).

MATERIALS AND METHODS

Grapes were collected from Grape research station University farm (area about half acre) through organic farming without pesticide spray to serve as Blank. Two separate plots of Grapes (area about half acre each) were sprayed with each pesticides and were harvested After two hours for determining the effect of various traditional processing techniques such as washing with Tap water, 2% salt solution, 2% tamarind solution, lemon water, Baking soda, Vinegar, Bio wash (available in market) and cooking etc. on the level of removal/reduction in pesticide residue contents.The pesticides, profenophos 50EC@ 2ml/lit,chlorpyrifos 20EC@ 2ml/lit, dimethoate 30EC @ 4ml/lit, malathion 50EC@3ml/lit, phosalone 35EC@3ml/lit, quinalphos 25EC@ 2ml/lit, triazophos 40EC @ 2.5ml/lit, lamdacyhalothrin 5EC@ 0.6ml/lit.were sprayed at recommended dose respectively with Knapsack sprayer. After about 2 hours the Grapes was harvested and packed in polyethylene bags and brought to the laboratory of Pesticide residues,Professor JayashankarTelangana state Agriculture University, Hyderabad for further processing.

Household Processing methods of Grapes Samples

The Grape samples were subjected to different traditional processing techniques such as

T1	Dipping in tap water for 10 minutes and washing under tap water for 30 sec
T2	Dipping in 2% salt solution for 10 min: 80 grams of table salt is added to 4 lts of water, and 1 kg Grapes sample dipped in salt water for 10 min.
T3	Dipping in 2% tamarind Solution for 10 min: 80 grams of tamarind is added to 4 lts of water, and 1 kg Grapes sample dipped in salt water for 10 min.
T4	Dipping in Lemon water (1Lemon/1lit) for 10min: Juice of 4 lemons is added to 4 lts of water, and 1 kg Grapes sample is dipped in lemon water for 10 min.
T5	Dipping in 0.1% Sodium Bicarbonate solution for 10min: 4 grams of sodium bicarbonate is added to 4 lts of water; 1 kg Grapes sample is dipped in solution for 10 min.
T6	Dipping in 4% Acetic acid solution for 1min: 160 ml of acetic acid is added to 4 lts of water; 1 kg Grapes sample dipped in the solution for 10 min.
T7	Washing with Bio wash keep it for 10min: 8 ml of commercial formula Bio wash is added to 4 lts of water and 1 kg Grapes sample is dipped in solution for 10 min.

Chemicals

Pesticide standards of high purity (97.4%) wereobtained from Sigma Aldrich, and Commercialpesticides were purchased from local marketHyderabad-. The solvents of HPLCgrade were acetonitrile, n-hexaneobtained from Merck Germany. All the other chemicals and solvents of Analytical grade were obtained from Merck, Mumbai (India). Primary secondary amine (PSA, 40 lm, Bondesil), Analytical-grade sodium chloride and anhydrous magnesium sulphate was procured from Agilent scientific (Lake Forest CA 9630). Stock solutions (1,000 µg ml^{-1}) were prepared by dissolving reference standards in acetonitrile.

Extraction and Cleanup of pesticide residue analysis

After 10min of each treatment, Grape samples were taken out and air dried for 5 min. Grape samples were analyzed for Dimethoate, Profenophos, Chlorpyrifos, Malathion, Phosalone, Quinalphos, Triazophos, Lambda cyhalothrin pesticide residues following the AOAC official method 2011 (QuEChERS).after validation of the method at the laboratory. The samples were homogenized with robot coupe blixer, and homogenized 15±0.1g sample was taken in 50ml centrifuge tube. Then added with 30±0.1 ml acetonitrile. Sample is homogenized at 14000-15000 rpm for 2-3 min using Heidolph silent crusher and then added with 3±0.1g sodium chloride and mixed by shaking gently followed by centrifugation for 3 min at 2500-3000 rpm to separate the organic layer. The top organic layer of about 16 ml was taken into the 50 ml centrifuge tube and added with 9±0.1g anhydrous sodium sulphate to remove the moisture content. 8 ml of extract was taken in to 15 ml tube, containing 0.4±0.01gr PSA sorbent (for dispersive solid phase d-SPE cleanup) and 1.2±0.01gr anhydrous magnesium sulphate. The sample tube was vortexed for 30sec then followed by centrifugation for 5min at 2500-3000rpm. The extract of about 2ml was transferred into test tubes and evaporated to dryness using turbovap with nitrogen gas and reconstituted with 1ml n-Hexane for GC analysis with ECD detector.

Estimation

The cleaned extracts were analyzed on Shimadzu 2010 GC equipped with Phenominexcapillary columns using ^{63}Ni electron capture detector (ECD) and nitrogen-phosphorous detector (NPD). Operating conditions were as per details: Detector : ECD (^{63}Ni), column: Phenominex MR1 column of 5% diphenyl/ 95% dimethyl fused silica capillary column (30 m×0.25 mm ID, 0.25 μm film thickness) with split system. Temperatures (^0C):150 ^0C (5 min) →5 ^{0} min $^{-1}$ → 190 ^0C (2 min) → 15 ^{0} min $^{-1}$ 280 ^0C (10 min); injection port: 280 ^0C; detector: 300 ^0C; carrier gas: (N_2), flow rate 60 ml min^{-1}, 2 ml through column and split ratio 1:10. Carrier gas, N_2, flow rate 60 ml min^{-1}, 2 ml through column. ForOPs: Detector: FPD, column: Phenominex MR1 column of methyl silicone (10 m×0.53 mm ID, 2.65 μm film thickness). Temperatures(^0C): Oven: (^0C):150 ^0C (5 min) → 5 ^{0} min $^{-1}$ → 190 ^0C (2 min) → 15 ^{0} min $^{-1}$ 280 ^0C (10 min); injection port: 280 ^0C; detector: 300 ^0C; carrier gas N_2 60 ml min^{-1}, H_2, 1.5 ml min^{-1} and zero air 130 ml min^{-1}.

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RESULTS AND DISCUSSIONS

The residues of dimethoate, profenophos, chlorpyrifos, malathion, phosalone, quinalphos, triazophos Lambda cyhalothrin in Grape samples have got substantial reduction by different house hold processing methods. The reduction percentage and residue levels have been presented in Table 2.

In the process of washing under running tap water malathion residues were reduced up to 50.90%, whereas phosalone 55.40%, Quinolphos 56.10%, Lambda cyhalothrin 43.0% ,Profenophos 49.8%., Chlorpyriphos 28.0%, and dimethoate were reduced to 53.40% .By washing the Grapes samples under running tap water the residue levels of Chlorpyrifos were not degraded much. With the method of 2 % tamarind solutionQuinalphos residues were reduced up to 80.40%. The 2 % tamarind solution method has shown better effect when compared with Tap water washing. By washing with 2 % tamarind solution Dimethoate residues reduced by 58.80%, Quinalphos 80.4%, Profenophos 57.6%,Phosalone 66.6%, and the lowest reduction was seen in Chlorpyrifos 25.8% residues. Among all the treatments washing with 0.1% sodium bicarbonate solution ,4% acetic acid solution, were less effective in reducing the pesticide residues compared to washing with tap water, lemon water, washing methods utilized. Among all the methods utilized 2 % tamarind solution and washing with 2% salt solution were most effective.

Table 1: Pesticide Residues (mg/kg) Grape Samples collected at 2 hrs after spray CONTROL

Table:1 Pesticide Residues (mg/kg) in Grape Samples collected at 2 hrs after spray CONTROL								
	Residues (mg/kg)						MRL (mg/kg)	
Pesticide	R1	R2	R3	AVERAGE	SDEV	% RSD	FSSAI	CODEX
Dimethoate	1.816	1.467	1.785	1.689	0.083	4.885	2	NA
Chlorpyriphos	4.356	4.521	4.442	4.440	0.034	0.763	0.5	0.5
Quinolphos	0.931	0.882	0.866	0.893	0.017	1.931	NA	NA
Profenophos	1.411	1.399	1.377	1.396	0.012	0.890	NA	NA
Phosalone	1.599	1.578	1.577	1.585	0.007	0.420	5	NA
Lamda cyhalothrin	2.277	2.281	2.268	2.275	0.006	0.242	NA	NA
Malathion	0.149	0.158	0.159	0.155	0.006	3.546	4	5
Triazophos	1.988	1.898	1.864	1.917	0.064	3.343	NA	NA

Table 2: % removal of pesticide residues over control

Pesticide	% removal of pesticide residues over control						
	Tap Water	Lemon water	Tamarind solution	2% salt solution	0.1% sodium bicarbonate solution	4% Acetic Acid solution	BIO WASH
Dimethoate	53.4	45.0	58.8	44.1	58.2	59.8	51.5
Chlorpyriphos	28.0	24.4	25.8	23.5	39.0	36.5	23.6
Quinolphos	56.1	56.5	80.4	66.3	77.0	79.5	58.4
Profenophos	49.8	46.1	57.6	43.0	62.0	60.0	46.6
Phosalone	55.4	50.3	66.6	44.5	65.4	76.2	50.7
Lamdacyhalothrin	43.0	44.0	61.0	42.3	59.5	67.5	45.9
Malathion	50.9	44.6	78.5	52.4	56.2	70.0	53.2
Triazophos	40.1	33.5	46.1	32.9	45.4	51.6	32.3

Pesticides are used indiscriminately and excessively throughout the globe, and these residues remain in the food materials, water, fruits, vegetables (Baptista et al.,2008, Lazic et al., 2009) and in total diet. Excessive use of pesticides, their toxic residues has been reported in various environmental commodities (Lazic et al.,2009). These pesticide residues enter in to the human body by consumption of the pesticide contaminated food which leads to the chronic disorders. Thus the removal of these residues from food commodities utilizing different processing methods is very essential)The different house hold preparations such as washing with tap water, washing with lemon water, dipping in 2% tamarind solution, cooking, dipping

in 2% salt solution. Washing with 4% acetic acid solution, biowash play a role in the reduction of pesticide residues (WasimAktar et al.,2010). Thus, based on the results obtained in this study it can be concluded that by processing the grapesl with the traditional processing methods if it helps in the removal of pesticide residues below MRL levels, then it is safe for human consumption. The results of earlier workers (Dhiman et al., 2006, Kumari.2008, WasimAktar et al., 2010, Saghir A. et al., 2012.) have shown similar results reducing the pesticide residues from brinjal and other vegetables.

CONCLUSIONS

From these household processing, it is therefore concluded that water soluble contact pesticides residues such as Oragano phosphate pesticides can successfully be removed from Grapes by 2% salt solution and/or by 2 % Tamarind solution. Grapes consumers are advised to take after treatment of properly being washed for at least 10 minutes in salt.

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